(Porphinato)iron-Catalyzed Addition Reactions of Thiols to Alkenes via (σ-Alkyl)iron(II) Complexes

Masayuki Takeuchi, Hisashi Shimakoshi, and Koji Kano*

Department of Applied Chemistry, Faculty of Engineering, Doshisha University, Kamikyo-ku, Kyoto 602, Japan

The Markovnikov-type addition of thiols (derived from the corresponding disulfides) to alkenes occurs in anaerobic benzene–ethanol solutions containing NaBH$_4$ and (porphinato)iron(III) chloride (Por–Fe^{III}Cl). For example, the reaction of styrene with diphenyl disulfide affords phenyl 1-phenylethyl sulfide. It has been assumed that the hydride transfer from BH$_4^-$ to styrene yields 1-phenylethanide which is stabilized by coordinating to Por–Fe^{II} and that the resulting (σ-alkyl)iron(II) complex having a carbanion character reacts with diphenyl disulfide to give phenyl 1-phenylethyl sulfide and the thiophenolate ion.

Metalloporphyrins catalyze numerous reactions such as epoxidation and hydroxylation of alkenes,[1] hydroxylation of alkanes,[2] cyclopropanation of alkenes,[3] Diels–Alder reactions,[4] decomposition of amides,[5] oxidative decarboxylation of carboxylic acids,[6] polymerization,[7] and so on. One of the features of metalloporphyrins as catalysts is that a wide variety of compounds can coordinate with the metalloporphyrins as axial ligands. Recently, we reported the (porphinato)iron-mediated reduction of alkenes and alkynes by BH$_4^-$ in benzene–ethanol, where the (σ-alkyl)iron(III) and (σ-alkyl)iron(II) complexes have

Table 1. (PP)Fe-Catalyzed Reactions of Alkenes with Diphenyl Disulfide in Benzene–Ethanol (1:1) Containing NaBH$_4$ at Room Temperature

entry	substrate	reaction time/h	product	yield/%[a]
1	Ph—//	2	Ph—⟨(SPh)	28(65)
2	Ph—⫝̸	2	Ph—⊢—SPh	25(43)
3	Ph—⫝̸(Ph)	2	Ph—⊢—SPh (Ph)	22(35)
4	Ph⌒⫝̸—Ph	2	Ph⌒⌄Ph (SPh)	21(70)
5	Ph⌒/⌒Ph	2	Ph⌄⌄Ph (SPh)	14(67)
6	Ph⌒⫝̸⌄CH$_3$ (*cis* : *trans* = 1:1)	2	Ph⌒⌄ (SPh)	21(51)
7	(indene)	2	(indane-SPh)	23(68)
8	(cyclohexene)	2	(cyclohexyl-SPh)	7
9	(norbornene)	2	(norbornyl-SPh)	6
10	Ph—//	24	Ph—/	1(2)
			Ph⌄⌄Ph	10(15)

[a] Yields based on an initial concentration of the substrates. The values in parentheses are the yields based on the consumed substrates.

been assumed as the intermediates having the nature of an alkyl radical and a carbanion, respectively.[8] The (σ-alkyl)iron porphyrin complexes can be prepared by several methods[9] and are intermediates in reductive dehalogenation of halotanes[10] and oxygenation of alkenes.[11]

In a previous communication,[12] we briefly reported the addition of thiophenol (the origin of thiophenol is diphenyl

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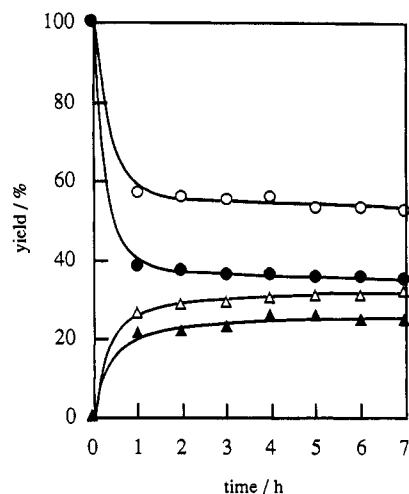(12) Kano, K.; Takeuchi, M.; Hashimoto, S.; Yoshida, Z.-i. *Chem. Lett.* **1990**, 1381.

Figure 1. Reactions of styrene (O, △) and 1,1-diphenyleth-ylene (●, ▲) with diphenyl disulfide in N₂-saturated benzene–ethanol (1:1) containing (PP)Fe^{III}Cl and NaBH₄. The reaction conditions were shown in the text. Both conversion of the alkenes (O, ●) and yields of the thiophenol adducts (△, ▲) were leveled off after 2 h.

Table 2. (PP)Fe-Catalyzed Reactions of Styrene with Disulfides, Thiophenol, and the Thiophenolate Ion in Benzene–Ethanol (1:1) Containing NaBH₄ at Room Temperature[a]

entry	disulfide or thiol	reaction time/h	product	yield/%[b]
1	Ph-SS-Ph	24	Ph—⟨SPh	38(74)
2	Ph-SH	24	Ph—⟨SPh	2(90)
3	Ph-SNa[c]	24	Ph—⟨SPh	11(20)
4	CH₃-SS-CH₃	24	Ph—⟨SCH₃	24(64)
5	C₂H₅-SS-C₂H₅	24	Ph—⟨SC₂H₅	26(36)

[a] The reaction conditions were shown in the Experimental Section [mol ratio: (PP)Fe^{III}Cl:styrene:NaBH₄:(C₆H₅S–)₂ = 1:10:20:10, (PP)-Fe^{III}Cl:styrene:NaBH₄:C₆H₅SH or C₆H₅S⁻ = 1:10:20:20]. [b] Yields based on an initial concentration of styrene. The values in parentheses are the yields based on the consumed styrene. [c] The thiophenolate anions are prepared by the reaction of thiophenol with equimolar NaH.

disulfide) to styrene catalyzed by (PP)Fe (PP: protoporphyrin IX dianion) in N₂-saturated benzene–ethanol containing NaBH₄. The (σ-alkyl)iron porphyrin complex has also been assumed as an intermediate.[12] The present paper deals with the details in the (porphinato)iron-catalyzed addition of thiols to alkenes and the reaction mechanism involving the (σ-alkyl)iron(II) porphyrins as the intermediates. The (σ-alkyl)iron(II) porphyrin complexes may act as the nucleophiles which attack the disulfides to give the thiol adducts and the thiolate anion.
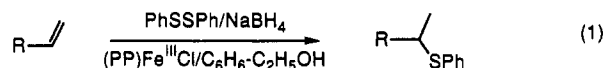
Results

(PP)Fe-Catalyzed Reactions. In the absence of (porphinato)iron, styrene (1.53 mmol) does not react with diphenyl disulfide (1.53 mmol) in N₂-saturated benzene–ethanol (1:1) containing NaBH₄ (3.06 mmol). However, the addition of ferriprotoporphyrin IX chloride ((PP)Fe^{III}-Cl, 0.153 mmol) to this system promotes the addition of

Table 3. (TPP)Fe-Catalyzed Reactions of Alkenes with Diphenyl Disulfide in Benzene–Ethanol (1:1) Containing NaBH₄ at Room Temperature

entry	substrate	reaction time/h	product	yield/%[a]
1	Ph—/	2	Ph—⟨SPh	19(22)
			Ph—/	26(30)
			Ph—⟨(/Ph)	21(25)
2[b]	Ph—/	2	Ph—⟨SPh	18(42)
			Ph—/	3(7)
			Ph ⟩O-N⟨	8(19)
3	Ph—⟨	2	Ph—|—SPh	23(23)
			Ph—⟨	25(25)
			Ph—|—|—Ph	42(42)
4	Ph⌒⌒Ph	2	Ph⌒⟨SPh Ph	15(35)
			Ph⌒⌒Ph	15(35)
5	Ph⌒⌒Ph	2	Ph⌒⟨SPh Ph	9(21)
			Ph⌒⌒Ph	9(21)
6	Ph₂C=CH₂ (Ph Ph)	2	Ph—|—SPh Ph	19(29)
			Ph₂CH-CH₃ (Ph Ph)	39(60)
7	(norbornene)	2	(norbornyl-SPh)	3

[a] Yields based on an initial concentration of the substrate. The values in parentheses are the yields based on the consumed substrates. [b] In this system, the reaction was carried out in the presence of TEMPO (100 mol % toward styrene).
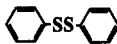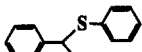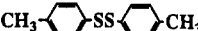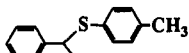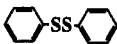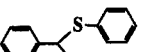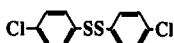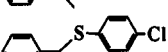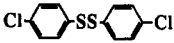
thiophenol to styrene (Table 1):

$$ R{-}/\ \xrightarrow[\text{(PP)Fe}^{III}\text{Cl/C}_6\text{H}_6\text{-C}_2\text{H}_5\text{OH}]{\text{PhSSPh/NaBH}_4}\ R{-}\langle_{\text{SPh}} \qquad (1) $$
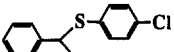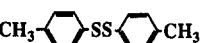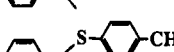
The reactions can be regarded as Markovnikov-type additions of thiophenol to the alkenes. Alkenylbenzenes such as styrene, 1-methylstyrene, 1,1-diphenylethylene, cis- and trans-stilbenes, and 2-methylstyrene give the corresponding adducts in 14–28% yields (entries 1–6), while the yields of the adducts of cyclic alkenes such as 1-methylcyclohexene and norbornene are very low (entries 8 and 9). Indene, a cyclic alkene, shows the same reactivity as those of the styrene derivatives (entry 7). It seems, therefore, that conjugation of the carbon–carbon double bond with the phenyl ring is important in promoting this addition reaction. In the case of styrene, the reduction products, ethylbenzene and meso- and (±)-2,3-diphenyl-butane, were obtained in low yields when diphenyl disulfide was removed from the reaction system (entry 10).

In each case, the conversion of the alkene as well as the yield of the adduct was leveled off after ca. 1 h (see Figure

Table 4. Competing Reactions of Styrene with Two Kinds of Diphenyl Disulfides in Benzene–Ethanol (1:1) Containing NaBH₄ at Room Temperature[a]

entry	disulfide	reaction time/h	product (yield/%[b])	relative rate
1	PhSS-Ph / CH₃-C₆H₄-SS-C₆H₄-CH₃	1	Ph-CH(CH₃)-S-Ph (13) / Ph-CH(CH₃)-S-C₆H₄-CH₃ (15)	$\dfrac{p\text{-H}}{p\text{-CH}_3} = 0.87$
2	PhSS-Ph / Cl-C₆H₄-SS-C₆H₄-Cl	1	Ph-CH(CH₃)-S-Ph (13) / Ph-CH(CH₃)-S-C₆H₄-Cl (43)	$\dfrac{p\text{-Cl}}{p\text{-H}} = 3.3$
3	Cl-C₆H₄-SS-C₆H₄-Cl / CH₃-C₆H₄-SS-C₆H₄-CH₃	1	Ph-CH(CH₃)-S-C₆H₄-Cl (28) / Ph-CH(CH₃)-S-C₆H₄-CH₃ (12)	$\dfrac{p\text{-Cl}}{p\text{-CH}_3} = 2.3$

[a] The mixture of styrene (1.5 mmol), two kinds of diphenyl disulfides (0.75 mmol of each), (TPP)Fe^{III}Cl (0.15 mmol), and NaBH₄ (3.0 mmol) in N₂-saturated benzene–ethanol (1:1, 8 mL) was stirred at room temperature. [b] Yields based on an initial concentration of the substrate.

1). Such saturation phenomena in the addition reaction are due to the decomposition of BH₄⁻ prior to complete consumption of the alkene. Further addition of NaBH₄ reinitiates the addition reaction. The final yield of phenyl 1-phenylethyl sulfide was 75% when the reaction of styrene with diphenyl disulfide was carried out at 2 °C and additional NaBH₄ was added after 24 h (see Experimental Section). After saturation, a small amount of the reaction mixture (entry 1) was added into N₂-saturated pyridine (py) to measure the electronic absorption spectrum. Absorption maxima were observed at 524.6 and 556.6 nm, indicating the formation of (PP)Fe^{II}(py)₂.[13] Judging from the extinction coefficient, (PP)Fe^{II}(py)₂ was formed in 88% yield at 24 h. This means that, at least, the porphyrin ring of the catalyst is not damaged seriously during the reaction.
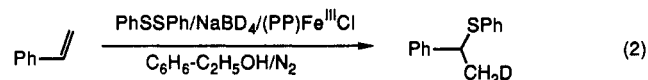
Besides diphenyl disulfide, dialkyl disulfides such as dimethyl disulfide and diethyl disulfide also provide the corresponding adducts (Table 2). However, both thiophenol and the thiophenolate ion scarcely provide the thiophenol adduct of styrene (entries 2 and 3).

(TPP)Fe-Catalyzed Reactions. (TPP)Fe (TPP: 5,10,15,20-tetraphenylporphyrin dianion) also acts as a catalyst for the reactions of the alkenes with diphenyl disulfide. Table 3 summarizes the results. The characteristic of the (TPP)Fe-catalyzed reaction is that the reduction of the alkene to the alkane(s) occurs competitively. In the previous paper,[8] we reported the (porphinato)iron-mediated reduction of the alkenyl- and alkynylbenzenes with NaBH₄ in protic solvent. (TPP)Fe^{III}-CH(CH₃)(C₆H₅) and [(TPP)Fe^{II}CH(CH₃)(C₆H₅)]⁻, which are (σ-alkyl)iron complexes, have been postulated as the precursors of 2,3-diphenylbutane and ethylbenzene, respectively, in the (TPP)Fe-mediated reduction of styrene.[8b] It may be reasonable to assume that the (σ-alkyl)iron complex is also an intermediate in the addition reaction.

(TPP)Fe^{II}-Catalyzed Reactions of Styrene. The formation of (TPP)Fe^{II}(HOC₂H₅)₂ was detected by means of electronic absorption spectroscopy (λ_{max} = 428, 540, 553 (sh), and 602 nm)[14] when a mixture of (TPP)Fe^{III}Cl, NaBH₄, and diphenyl disulfide was dissolved in N₂-

saturated benzene–ethanol (see Experimental Section). Diphenyl disulfide was essential for forming (TPP)-Fe^{II}(HOC₂H₅)₂. After all (TPP)Fe^{III}Cl was converted to (TPP)Fe^{II}(HOC₂H₅)₂, styrene in N₂-saturated benzene–ethanol was added into the (porphinato)iron(II) complex solution ((TPP)Fe^{II}(HOC₂H₅)₂:NaBH₄:(PhS)₂:styrene = 1:1000:250:125 in mol ratio). After 6 h, phenyl 1-phenylethyl sulfide (4%, turnover number, TN = 5) and ethylbenzene (5%, TN = 6) were formed in low yields. The low yields are ascribed to the use of the relatively small amounts of catalyst. As can be expected, the formation of 2,3-diphenylbutane is not detected. The present result clearly exhibits that the addition reaction takes place through the catalysis of the (porphinato)iron-(II), which also catalyzes the reduction of styrene to ethylbenzene.

Deuterium Incorporation. The deuterium incorporation in the formation of phenyl 1-phenylethyl sulfide from the reaction of styrene with diphenyl disulfide was studied by using C₂H₅OD and/or NaBD₄. The reaction conditions were the same as those of entry 1 in Table 1. After 24 h, the thiophenol adduct was isolated by silica gel column chromatography with hexane–benzene (15:1) and analyzed by means of GC–MS and ¹H NMR spectroscopies. Deuterium was incorporated into the thiophenol adduct to yield phenyl 2-deuterio-1-phenylethyl sulfide when NaBD₄ was used:

$$\text{Ph}\text{—CH=CH}_2 \xrightarrow[\text{C}_6\text{H}_6\text{-C}_2\text{H}_5\text{OH/N}_2]{\text{PhSSPh/NaBD}_4/\text{(PP)Fe}^{III}\text{Cl}} \text{Ph}\text{—CH(SPh)CH}_2\text{D} \quad (2)$$

The proton transfer from ethanol does not occur in this reaction. The hydride transfer from BH₄⁻ to styrene should yield a carbanion, 1-phenylethanide. Therefore, the result of the deuterium incorporation suggests that the addition reaction formally proceeds via an electrophilic attack of 1-phenylethanide, (C₆H₅CHCH₃)⁻, on diphenyl disulfide. If thiophenol produced by the reduction of diphenyl disulfide with sodium borohydride adds to styrene, the adduct without the deuterium should be formed in the reaction using NaBD₄ because the fast H–D exchange between C₆H₅SD and C₂H₅OH occurs. Probably, the hydride transfer from BH₄⁻ to styrene proceeds indirectly. We are assuming that a hydride complex of (TPP)Fe^{II},

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Table 5. ¹H NMR^a and GC-MS^b Data for the Products

compound	¹H NMR, δ (ppm)	GC-MS, m/z
	1.57 (d, 3H, –CH₃) 1.91 (s, 3H, –SCH₃) 3.85 (q, 1H, –CH) 7.32–7.33 (5H, Ph)	152 (64, M⁺) 137 (5, M⁺ – CH₃) 105 (100, M⁺ – SPh)
	1.16 (t, 3H, –SCH₂CH₃) 1.57 (d, 3H, –CH₃) 2.32 (m, 2H, –SCH₂CH₃) 3.98 (q, 1H, –CH) 7.23–7.33 (5H, Ph)	166 (24, M⁺) 105 (100, M⁺ – SPh) 77 (20, Ph)
	1.61 (d, 3H, –CH₃) 4.33 (q, 1H, –CH) 7.20–7.29 (10H, Ph)	214 (8, M⁺) 109 (9, SPh) 105 (100, M⁺ – SPh)
	1.60 (d, 3H, –CH₃) 2.30 (s, 3H, –C₆H₅CH₃) 3.85 (q, 1H, –CH) 7.17–7.27 (9H, Ph)	228 (12, M⁺) 124 (34, SC₆H₅CH₃ + 1) 105 (100, M⁺ – SPh)
	1.62 (d, 3H, –CH₃) 4.29 (q, 1H, –CH) 7.17–7.26 (9H, Ph)	248 (2, M⁺) 105 (100, M⁺ – SPh)
	1.68 (s, 6H, –CH₃) 7.14–7.42 (10H, Ph)	228 (3, M⁺) 119 (100, M⁺ – SPh)
	1.94 (s, 3H, –CH₃) 7.0–7.40 (15H, Ph)	290 (13, M⁺) 181 (100, M⁺ – SPh)
	3.22 (m, 2H, –CH₂C₆H₅) 4.37 (t, 1H, –CH) 7.0–7.20 (15H, Ph)	290 (9, M⁺) 199 (100, M⁺ – CH₂C₆H₅) 181 (75, M⁺ – SPh)
	0.91 (t, 3H, –CH₂CH₃) 1.97 (m, 2H, –CH₂CH₃) 4.04 (m, 1H, –CH) 7.17–7.24 (10H, Ph)	228 (12, M⁺) 119 (100, M⁺ – SPh)
	2.21 (m, 1H, –CH(SPh)–CH₂–CH₂–) 2.53 (m, 1H, –CH(SPh)–CH₂–CH₂–) 2.86 (m, 1H, –CH(SPh)–CH₂–CH₂–) 3.02 (m, 1H, –CH(SPh)–CH₂–CH₂–) 4.76 (m, 1H, –CH(SPh)–) 7.15–7.40 (9H, Ph)	226 (4, M⁺) 117 (100, M⁺ – SPh)
	1.22 (s, 3H, –CH₃) 1.25–1.76 (10H, –CH₂–) 7.31–7.52 (5H, Ph)	206 (6, M⁺) 110 (100, SPh + 1)
	1.19–1.83 (8H, –CH₂–) 2.30 (m, 2H, norbornane 1,4-CH–) 3.18 (m, 1H, –CH(SPh)–) 7.14–7.27 (5H, Ph)	204 (19, M⁺) 95 (100, M⁺ – SPh)
	1.02 (s, 3H, TEMPO –CH₃) 1.16 (s, 3H, TEMPO –CH₃) 1.29 (s, 3H, TEMPO –CH₃) 1.36 (s, 3H, TEMPO –CH₃) 1.46–1.56 (6H, TEMPO –CH₂–) 1.77 (d, 3H, –CH₃) 4.77 (q, 1H, –CH) 7.22–7.31 (5H, Ph)	262 (0.3, M⁺) 157 (100, M⁺ – PhCH(CH₃)) 105 (40, M⁺ – TEMPO)

^a ¹H NMR spectra were measured in CDCl₃ (TMS). ^b The mass spectrum of 1-(1-phenylethoxy)-2,2,6,6-tetramethylpiperidine was measured by an EI method (70 eV).

[(TPP)Fe^{II}H]⁻, is the reducing agent of the alkenes, though no direct evidence has been obtained.

Competing Reactions of Diphenyl Disulfides with Styrene. If the addition proceeds via the nucleophilic

attack of 1-phenylethanide, which may be stabilized by coordinating with (TPP)Fe^{II}, on diphenyl disulfide, the electron-attracting groups attached to diphenyl disulfide should accelerate the addition reaction. Then the competing reactions using two kinds of 4,4'-disubstituted diphenyl disulfides were carried out. The results are shown in Table 4. The electron-attracting substituent accelerates the foramtion of the adduct while the effect of the electron-donating substituent is obscure.
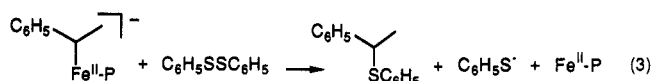
Effects of a Free-Radical Trap. Since a radical mechanism cannot be denied for the addition reaction, the effects of a free-radical trap on the reaction of styrene with diphenyl disulfide have been studied. TEMPO (2,2,6,6-tetramethylpiperidinyloxy) was used as the radical trap. The results are shown in Table 3 (entry 2). Comparing with the results of the experiment without TEMPO (entry 1 in Table 3), it becomes clear that (1) the rate of the styrene disappearance is decelerated by TEMPO, (2) the formation of 2,3-diphenylbutane is completely inhibited by TEMPO, (3) 1-(1-phenylethoxy)-2,2,6,6-tetramethylpiperidine (mp 43–43.5 °C) is formed instead of 2,3-diphenylbutane, (4) the yield of the thiol adduct calculated from the amounts of consumed styrene is much higher in the reaction in the presence of TEMPO than that in the absence of TEMPO, and (5) the yield of ethylbenzene in the presence of TEMPO is considerably lower than that in the absence of TEMPO. We have already found an inhibition effect of TEMPO on the formation of 2,3-diphenylbutane, which occurs via (TPP)-Fe^{III}CH(CH$_3$)C$_6$H$_5$ having a radical character.[8b] We also demonstrated in the previous paper that the weak effect of TEMPO on the formation of ethylbenzene can be ascribed to the nature of the precursor of ethylbenzene, [(TPP)Fe^{II}CH(CH$_3$)C$_6$H$_5$]$^-$, which has carbanion character and abstracts a proton from ethanol, yielding ethylbenzene.[8b] The total yield for ethylbenzene and the thiol adduct in the presence of TEMPO (49%) is almost comparable to that in the absence of TEMPO (54%). This may be explained as that both ethylbenzene and the thiol adduct are formed via the same reaction intermediate, [(TPP)Fe^{II}CH(CH$_3$)C$_6$H$_5$]$^-$, and the relative rates for formation of the thiol adduct and ethylbenzene are affected by TEMPO. In any event, it is clear that the formation of the thiol adduct is not inhibited by TEMPO, though the rate of formation is fairly reduced.

Discussion

The (TPP)Mn^{III}–BH$_4$$^-$–protic solvent system was applied for the first time in hydroxylation of cyclohexene with dioxygen by Tabushi and Koga.[15] The studies using similar systems have revealed that the oxygenation of the alkenes catalyzed by the manganese,[15,16] iron,[11,17] and cobalt complexes of TPP[18] yields corresponding ketones and/or hydroxylated products. No epoxides are formed in these reactions. The reaction of nitrobenzenes[19] and alkenes[8] and the addition of thiophenol to styrene[12] have also been achieved by the use of similar systems. In this study, we found that a variety of alkenylbenzenes reacts

with the disulfides such as dimethyl disulfide, diethyl disulfide, and diphenyl disulfide to afford the corresponding thiol adducts of the alkenes in benzene–ethanol containing NaBH$_4$ and (porphinato)irons. In the (PP)-Fe-catalyzed reaction of styrene with diphenyl disulfide, phenyl 1-phenylethyl sulfide was obtained in 75% yield (see Experimental Section). The (porphinato)iron-catalyzed addition of thiols to alkenylbenzenes may be used for syntheses of unsymmetrical sulfides.

For synthetic purposes, (PP)Fe^{III}Cl is better than (TPP)-Fe^{III}Cl because byproducts such as reduction products are not obtained from the (PP)Fe-catalyzed reactions. However, (TPP)Fe^{III}Cl is very convenient for studying the reaction mechanism of the addition reactions. The following discussion on the mechanism will focus on the styrene–diphenyl disulfide–(TPP)Fe^{III}Cl system unless otherwise noted. Recently, we demonstrated that the (σ-alkyl)iron porphyrin complexes, (TPP)Fe^{III}CH(CH$_3$)C$_6$H$_5$ and [(TPP)Fe^{II}CH(CH$_3$)C$_6$H$_5$]$^-$, are generated as the intermediates in the (TPP)Fe-mediated reduction of styrene with NaBH$_4$ in benzene–ethanol.[8b] It is quite reasonable to assume that the (porphinato)iron-catalyzed addition reaction of thiophenol to styrene also proceeds via the (σ-alkyl)iron porphyrin complex, because the conditions of the present reaction are the same as those of the (porphinato)iron-mediated reduction of styrene except for the existence of diphenyl disulfide. Since the present study shows that the thiophenol adduct is obtained from the catalysis by (porphinato)iron(II), [(TPP)Fe^{II}CH(CH$_3$)-C$_6$H$_5$]$^-$ having a carbanionic nature is assumed to be the precursor of the thiophenol adduct of styrene. The fact that the radical trap, TEMPO, strictly inhibits the production of 2,3-diphenylbutane while the formation of phenyl 1-phenylethyl sulfide is not inhibited by TEMPO clearly argues against the importance of the reaction of the 1-phenylethyl radical or of this radical stabilized by coordinating to (TPP)Fe^{II} with diphenyl disulfide or with the phenylthio radical (C$_6$H$_5$S$^{\bullet}$) in the pathway yielding the thiophenol adduct of styrene. The reaction of the phenylthio radical with styrene is also excluded from the mechanism because anti-Markovnikov-type additions are known to occur in this radical reaction.[20] The effects of TEMPO as well as the effects of the substituents attached to the 4- and 4'-positions of diphenyl disulfide on the addition reaction strongly suggest the nucleophilic attack of 1-phenylethanide on diphenyl disulfide, leading to the formation of the adduct and thiophenolate anion:

$$\underset{Fe^{II}\text{-}P}{\overset{C_6H_5}{\diagdown}} \Big]^- + C_6H_5SSC_6H_5 \longrightarrow \underset{SC_6H_5}{\overset{C_6H_5}{\diagdown}} + C_6H_5S^- + Fe^{II}\text{-}P \quad (3)$$

The fact that thiophenol itself (entry 2 in Table 2) and the thiophenolate ion (entry 3 in Table 2) scarcely afford the adduct supports the mechanism represented by eq 3. Formation of the thiophenol adduct in the reactions using thiophenol and the thiophenolate ion may be interpreted in terms of the formation of small amounts of diphenyl disulfide (which was detected by GLC) from thiophenol and its anion. 1-Phenylethanide should be stabilized by coordinating to (TPP)Fe^{II}. If free 1-phenylethanide is produced, the proton transfer from the protic solvent to this carbanion should occur to yield ethylbenzene in preference to the addition of the carbanion to diphenyl disulfide.

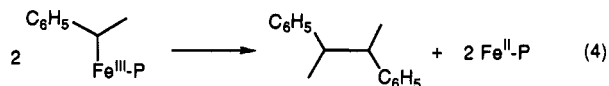(15) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* 1979, *101*, 6456.

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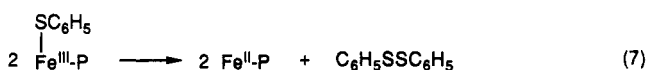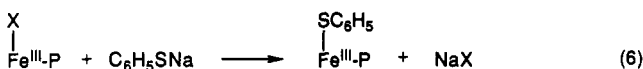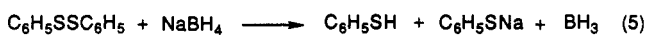
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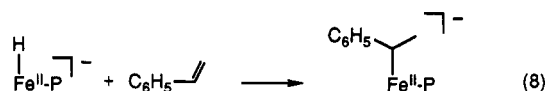(20) (a) Pallen, R.; Sivertz, C. *Can. J. Chem.* 1957, *35*, 723. (b) Sivertz, C. *J. Phys. Chem.* 1959, *63*, 34.

There are two possible pathways to yield [(TPP)Fe^{II}-$CH(CH_3)C_6H_5$]$^-$. The coupling reaction of (TPP)Fe^{III}-$CH(CH_3)C_6H_5$ affords 2,3-diphenylbutane and the (porphinato)iron(II) complex, which exists in the form of (TPP)$Fe^{II}(C_2H_5OH)_2$:[8b]

$$2 \quad \underset{Fe^{III}\text{-}P}{\overset{C_6H_5}{\diagdown}} \longrightarrow \underset{C_6H_5}{\overset{C_6H_5}{\diagup}} + 2\ Fe^{II}\text{-}P \quad (4)$$

The (porphinato)iron(II) complex serves to form the (σ-alkyl)iron(II) complex. This mechanism, however, cannot be applied to the (PP)Fe-mediated reaction because no coupling product is formed in this system. We found that (TPP)Fe^{II} is produced when diphenyl disulfide is added into the mixture of (TPP)Fe^{III}Cl and $NaBH_4$ in benzene-ethanol. The GLC analysis reveals the formation of thiophenol in the reaction of diphenyl disulfide with $NaBH_4$ in benzene-ethanol. These findings strongly suggest the occurrence of the following reactions:

$$C_6H_5SSC_6H_5 + NaBH_4 \longrightarrow C_6H_5SH + C_6H_5SNa + BH_3 \quad (5)$$

$$\underset{Fe^{III}\text{-}P}{\overset{X}{|}} + C_6H_5SNa \longrightarrow \underset{Fe^{III}\text{-}P}{\overset{SC_6H_5}{|}} + NaX \quad (6)$$

$$2\ \underset{Fe^{III}\text{-}P}{\overset{SC_6H_5}{|}} \longrightarrow 2\ Fe^{II}\text{-}P + C_6H_5SSC_6H_5 \quad (7)$$

where X$^-$ is $C_2H_5O^-$.[8b] It is known that both (TPP)Fe^{III}-SC_6H_5 and (PP)$Fe^{III}SC_6H_5$ are easily converted to the (TPP)Fe^{II} and diphenyl disulfide.[21,22] It may be considered that the (porphinato)iron(II) complex reacts with BH_4^- to form [(TPP)Fe^{II}H]$^-$ which reduces the alkene to give the (σ-alkyl)iron(II) porphyrin complex:

$$\underset{Fe^{II}\text{-}P}{\overset{H}{|}}\ \rceil^- + C_6H_5\diagup\!\!\!/ \longrightarrow \underset{Fe^{II}\text{-}P}{\overset{C_6H_5}{\diagdown}}\ \rceil^- \quad (8)$$

The reaction shown by eq 8 is followed by the nucleophilic substitution reaction between diphenyl disulfide and 1-phenylethanide (eq 3).

Experimental Section

Chemicals. (TPP)Fe^{III}Cl was prepared and purified according to the procedures described in the literature.[23] (PP)Fe^{III}Cl

(Sigma) was commercially obtained. All alkenes (reagent grade) were purchased (Nacalai) and used without further purification. Dimethyl disulfide, diethyl disulfide, diphenyl disulfide (Nacalai), 4,4'-dichlorodiphenyl disulfide (Tokyo Kasei), $NaBH_4$ (Nacalai), $NaBD_4$ (Aldrich), and C_2H_5OD (CEA) were commercially obtained. 4,4'-Dimethyldiphenyl disulfide (Tokyo Kasei) was recrystallized from benzene-methanol.

Measurements. All measurements were carried out by using the same instruments described in the previous paper.[8b]

General Procedures of the Addition Reaction. A typical example of the reaction of styrene with diphenyl disulfide is shown below. The mixture of (PP)Fe^{III}Cl (100 mg, 0.15 mmol), $NaBH_4$ (115 mg, 3.0 mmol), diphenyl disulfide (334 mg, 1.5 mmol), and biphenyl (25 mg, an internal standard for GLC) was placed in a 30-mL two-necked flask. The flask was sealed by a silicon cap and a three-way glass cock with a rubber balloon filled with the N_2 gas. The reaction vessel was evacuated by a water pump and then filled with the N_2 gas from the balloon. After the four evacuation-charging with N_2 cycles, styrene (160 mg, 1.5 mmol) in N_2-saturated benzene-ethanol (1:1, 8 mL) was injected into the vessel using a syringe and the mixture was stirred at room temperature. The progressive change of the reaction was followed by means of GLC. The thiophenol adduct, phenyl 1-phenylethyl sulfide, was isolated by silica gel column chromatography with hexane-benzene (15:1) and analyzed by means of IR, ^{1}H NMR, and GC-MS spectroscopies. The reactions for the other alkene-disulfide systems were carried out by the same procedures. The analytical data for the thiol adducts as well as the TEMPO adduct are summarized in Table 5.

In order to optimize the yield of phenyl 1-phenylethyl sulfide, the reaction was carried out at 2 °C. After 24 h, the yield of the thiophenol adduct was 59%. Additional $NaBH_4$ (1.5 mmol) was added into the reaction mixture, and the resulting mixture was further stirred for 1 h at 2 °C. The yield of phenyl 1-phenylethyl sulfide was increased to 75% by this procedure.

(TPP)Fe^{II}-Catalyzed Reaction. The mixture of (TPP)Fe^{III}-Cl (10 mg, 0.014 mmol), $NaBH_4$ (556 mg, 14 mmol), diphenyl disulfide (818 mg, 3.7 mmol), and biphenyl (25 mg) was placed in a 30-mL two-necked flask. After replacement of the atmosphere in the flask with the N_2 gas by the procedures described above, 8 mL of N_2-saturated benzene-ethanol (1:1) was injected by a syringe. Within 15 min, the color of the reaction mixture changed from reddish brown to bright red, suggesting the formation of (porphinato)iron(II). The absorption maxima of this solution were observed at 428, 540, 553 (sh), and 602 nm, which are in good agreement with those of (TPP)Fe^{II} to which the THF molecules coordinate as the axial ligands.[14] We concluded that (TPP)$Fe^{II}(C_2H_5OH)_2$ is formed. In the absence of diphenyl disulfide, the formation of (TPP)$Fe^{III}OC_2H_5$ was detected by means of visible absorption spectroscopy (λ_{max} = 418, 580, and 635 nm (sh)).[8b] The formation of (TPP)Fe^{II} is well interpreted in terms of the reactions expressed by eqs 5, 6, and 9. After all (porphinato)iron(III) was converted to (porphinato)iron(II), styrene (186 mg, 1.8 mmol) in N_2-saturated benzene-ethanol (1 mL) was added into the (porphinato)iron(II) complex solution. The reaction was followed by means of GLC (see Results).

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